

Curie Relaxations of the Ferroelectric Polymers ter(VDF/TrFE/CTFE) and co(VDF/TrFE)

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Beamline(s): X27C

Introduction: New polymers of terpolymers of VDF/TrFE/CTFE show large electromechanical strains (4%) in the paraelectric phase as well as large dielectric constants (100) and are promising materials for actuators and thin film capacitors for microelectronics. Using SAX/WAX scattering, the changes in crystalline phases in the Curie transition region and morphology are measured as a function of terpolymer composition and compared to copolymers of VDF/TrFE to elucidate the electromechanical strain mechanisms in the amorphous and crystalline phases.

Methods and Materials: The terpolymers of ter(VDF/TrFE/CTFE) were synthesized by the Chung group (Penn State Univ.) using a novel boron catalyst to yield polymers of controlled stoichiometric composition (1). The incorporation of CTFE introduces a conformational defect in the crystal that expands the lattice and due to this instability lowers the Curie Transition to a selected temperature of operation ranging from 80C down to room temperature. The CTFE concentration in the crystalline phase is key in setting the temperature of the Curie transition and its corresponding crystalline motions. Therefore the crystalline relaxations of the CTFE containing terpolymers are compared to those of copolymers of VDF/TrFE as a baseline reference to establish the effects of CTFE. The copolymers were supplied by the NUWC NPT.

Our major emphasis was to compare the changes in crystal phase and crystalline lamellae thickness due to the incorporation of CTFE in the terpolymer to that of the copolymer at the Curie transition. The resulting intimate relationship between crystal lattice spacing and crystal thickness over the temperature range including the Curie transition was obtained by simultaneously measuring the lattice spacing (4-5Angstroms) by wide-angle x-ray scattering and crystalline lamellae thickness (150 – 300Angstroms) by small angle x-ray scattering. By considering morphology of an alternating layered structure of crystalline lamellae and amorphous regions, the dimensions of both regions were obtained from SAX intensities.

Results: The results of the SAX/WAX study show distinctly different structural behavior for the crystal transitions for the ter and copolymers of VDF in the Curie temperature range. This is illustrated in Fig 1 for the 66/23.5/11.5 VDF/TrFE/CTFE terpolymer (crystallized 118°C) and Fig 2 for the 65/35 VDF/TrFE copolymer (crystallized 120°C) that show the total integrated SAX intensity and dimension of the combined crystalline and amorphous regions or long spacing L_B . The integrated intensity indicates the crystal density decrease occurring for the ferroelectric to paraelectric crystal phase transition for the terpolymer in the range of 20 to 24°C and a nearly constant value for L_B the crystalline and amorphous spacing in this region. In comparison, the integrated intensity for the copolymer indicates a Curie transition range of 80 to 100°C accompanied by a noticeable increase in the crystal amorphous spacing in passing thru the transition. The corresponding crystal lattice d-spacings for the ferro to paraelectric crystal transition increase by 4% for the terpolymer and 10% for the copolymers for the temperatures shown. The lack of sensitivity of the long period spacing of the terpolymer to account for the above change in lattice d-spacing may indicate that the Curie transition even if induced by electric field may not be the major contribution to its large electrostriction. To complete this study SAX/WAX intensity profiles are being taken a terpolymer of a higher Curie temperature of 58°C to account for a greater range of transition behavior to better determine the sensitivity of the long period.

The larger lattice spacing d-spacings for the terpolymer over that of the copolymer and the lower values of the terpolymer integrated intensities indicate a lower crystal density for the terpolymer and corroborate that the CTFE moiety occurs in the crystalline regions. Due to this lower density, the CTFE defects in the terpolymer crystals are more mobile than the regioregular defects of the copolymer as indicated by an order of magnitude greater change in melting point shifts with crystallization temperatures. This indicates that the electrostriction may be sensitive to the CTFE concentration in the crystal and further work is needed to determine this sensitivity for optimizing terpolymer thermal processing conditions.

Conclusions: The lack of sensitivity of the long period spacing of the terpolymer to account for the above change in lattice d-spacing may indicate that the Curie transition even if induced by electric field may not be the major contribution to its large electrostriction.

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References:

- 1) M Chung and A. Petchsuk, "New Ferroelectric VDF/TrFE/CTFE Terpolymers with High Dielectric constant and Large Electrostriction Response at Ambient Temperature," U.S. Navy workshop on Acoustic Transduction Materials and Devices, 14-16 May 2001, Baltimore, MD
- 2) E. Balizer, Z. Wang, A. Petchsuk, B. Hsiao and M Chung. "Structural Relaxations of VDF/TrFE/TCFE Terpolymers," U.S. Navy workshop on Acoustic Transduction Materials and Devices, 14-16 May 2001, Baltimore, MD
- 3) Z. Wang, E. Balizer, B. Hsiao, C. Han. "The Structure Evolution During the Ferroelectric Phase Transition in Vinylidene Fluoride/TriFluoroethylene Copolymer, ACS Proceedings (Polymer Division), 12 –14 April 2002, Orlando, FL.

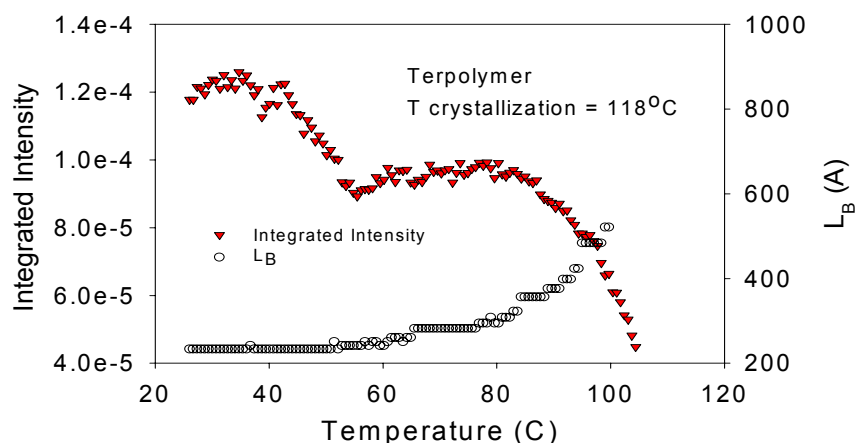


Figure 1. [graph: integrated intensity and L_B for the 66/22.5/11.5 terpolymer at a crystallization temperature of 118°C]

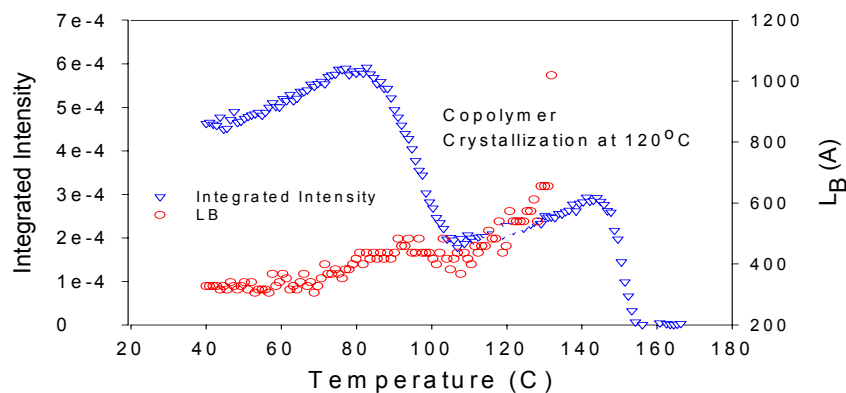


Figure 2. [graph: total integrated small angle scattering intensity and long period L_B for 65/35 mole % VDF/TrFE copolymer for crystallization temperature 120°C]